PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PWB-P2078PC0	**FOR FURTHER ACTION** See Form PCT/IPEA/416	
International application No. PCT/EP2004/051709	International filing date *(day/month/year)* 04.08.2004	Priority date *(day/month/year)* 07.08.2003
International Patent Classification (IPC) or national classification and IPC C08G18/08, C08G18/66, C08G18/65, C08G18/83, G03F7/038, C08K5/1515, C08L75/16		
Applicant HUNTSMAN ADVANCED MATERIALS (SWITZERLAND) GMBH et		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 16 sheets, as follows:
      - ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      - ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.

   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
24.02.2005	10.11.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Mader, M Telephone No. +49 89 2399-7537

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/051709

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

3, 4, 6-8, 14-16, 19, 22-34	as originally filed
1, 2, 2a, 5, 9-13, 17, 18, 20, 21	filed with the demand

Claims, Numbers

1-16	received on 24.09.2005 with letter of 20.09.2005

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	7-16
	No:	Claims	1-6
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: WO 02/094904 A (KOYANAGI HIROO ; OZAKI TORU (JP); TANAKA RYUTARO (JP); NIPPON KAYAKU K) 28 November 2002 (2002-11-28)

D2: US-A-4 877 711 (AOAI TOSHIAKI ET AL) 31 October 1989 (1989-10-31)

D3: EP-A-0 480 251 (BASF AG) 15 April 1992 (1992-04-15)

D4: US-B-6 417 2431 (PEETERS STEPHAN ET AL) 9 July 2002 (2002-07-09)

1. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-6 is not new in the sense of Article 33(2) PCT.

   D1 discloses a polyurethane soluble in aqueous alkali solutions for photosensitive resin compositions. It is prepared by reacting (A) an epoxy-carboxylate compound, (B) a diisocyanate, (C) a carboxylic acid having 2 OH groups, (D) a further diol compound and (E) an epoxy compound having ethylenically unsaturated groups (abstract). In the document JP2003268067, which is a family member of D1, the epoxy compound having ethylenically unsaturated groups is designated (D). From the examples, paragraph [0045] of the computer translation of said latter document, it appears that a polyurethane containing carboxyl groups is first prepared from (A), (B) and (C). Further on, this compound is reacted with (D) an epoxy compound which has an ethylenically unsaturated group (paragraph [0045] of the computer translation). It is assumed that this compound would react, in exactly the same way as in the present application, with the free carboxylic groups. The family member JP2003268067 furthermore discloses a photosensitive resin composition comprising the polyurethane mentioned above, (F) a photoinitiator and (G) a cross-linking agent. Further, said translation describes in paragraph [0042] a printed wired board obtained by coating the photosensitive composition onto a substrate, drying, irradiation through a photomask and developing. Optional further heat-treating is also mentioned. For development, an alkali solution such as sodium carbonate is suitable (paragraph [0043]).

Since the wording "obtained from (I), (ii) and (iii)" has been replaced by "obtained from monomers **comprising** (I), (ii) and (iii)", the presence of an epoxy-carboxylate compound such as compound (A) of D1 is no longer excluded in claim 1. The present wording of claim 1 refers to monomers (ii) which are already esterified with an olefinically unsaturated glycidyl ester, while in D1 this modification takes place after polymerization. However, the resulting linear polyurethane is structurally identical to the one used in D1. Therefore, claim 1 is anticipated by D1.
According to paragraph [0026] of the computer translation, poly glycidyl compounds are suitable as cross-linking agents (G). A further hardening component (H) is described in paragraphs [0027] and [0028], for example a phenol novolak mould epoxy resin, which could be regarded to represent the polymeric binder (A6) of present claim 2. Therefore claims 2-5 are not new in comparison to D1. Since, according to the abstract of D1, a further diol can be included into the resin composition, claim 6 is not novel in the light of D1.

2. Claims 1-8 differ from D3 or D4 in that a component ii) or b) which is an aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded, and some or all of said carboxyl groups have been esterified with an olefinically unsaturated C_3-C_8 alcohol or with the glycidyl ester of an olefinically unsaturated C_3-C_8 carboxylic acid, is used in said claims. They are therefore new over D3 as well as over D4.
Claims 7 and 8 differ from D1 in that a polyesterdiol, polycarbonatediol or a diol based on polybutadiene or polyisoprene is included in the linear polyurethane. Therefore claims 7 and 8 are new over D1.

Claims 9-16 relate to compositions comprising the polyurethanes of claim 7 or 8 and are hence new over D1, D3 or D4.

3. D2, which is regarded to represent the closest prior art, describes in synthesis example 12 of table 1, columns 15 to 16 a polyurethane prepared by reacting MDI, IPDI and dimethylol propionic acid (DMPA) (cf. also synthesis example 1, column 10), which is later on modified with glycidyl methacrylate. From synthesis example 1, describing the general procedure, it is clear that the polyurethane comprising carboxylic groups is isolated before the addition of the glycidyl compound.

Claim 7 differs from D2 in that in the preparation of the polyurethane, a component c) which is a polyesterdiol, a polycarbonatediol, a polylactonediol or a diol based on polybutadiene or polyisoprene, is additionally used. It is therefore new over D2 (Article 33(2) PCT).

The applicant shows in comparative examples that the use of a diol based on polybutadiene or polyisoprene leads to an increased thermal shock resistance. The problem to be solved by this alternative included in the subject-matter of claim 7 can therefore be regarded as providing polyurethanes with a high thermal shock resistance. Since none of D1-D4 suggest the usage of a diol based on polybutadiene or polyisoprene, an inventive step can be acknowledged for claim 7 as far as it concerns the usage of said compound.

However, the applicant does not show any similar effect when a polyester, polycarbonate or polylactone is used. The problem to be solved by those alternatives can therefore be regarded as the provision of alternative polyurethanes. The use of polyesters in polyurethanes based on a polyisocyanate and a diol comprising a carboxyl group such as dimethylol propionic acid is shown in D3 (column 2, lines 5-28; column 3, lines 2-10; example 1 in column 14; column 6, lines 13-24). Since the polyurethanes of D2 are merely chemically modified (after the polymerization) versions of the polyurethanes of D3, the skilled person would readily include the polyesters of D2 into the polyurethanes of D3 in order to solve the problem posed.

Therefore claim 7 does not involve an inventive step over D2 in combination with D3 (Article 33(3) PCT).

The same applies to claim 8, as D2 contemplates the use of a further aliphatic diol (column 5, lines 3-14). Light-sensitive solutions produced from the polyurethanes of D2 are disclosed in column 19, lines 30-40. They comprise a photoinitiator and a diluent. Other resins may also be mixed into the light-sensitive composition (column 5, lines 44-46). Therefore also claims 9 and 10 are not inventive (Article 33(3) PCT). Claims 15 and 16 are also not inventive since in both D2 (example, column 19, lines 22-25) and D3 (claim 3), the polymers are coated onto a substrate. Further, claims 11-13 do not involve an inventive step because the use of such crosslinking agents is

generally known in the art.
Claim 14 does not involve an inventive step (Article 33(3) PCT), as it is obvious for the skilled person that a curable polyurethane composition can also be used for mouldings. The applicant did not include any examples showing that mouldings derived from the described compositions provide any surprising effect.

4. The amendments carried out consist in
1. combining claims 12, 3 and 5 and replacing the expression "obtained from" by "obtained from monomers comprising" to give new claim 1,
2. renumbering claims 4 and 6-9 to give new claims 2-6,
3. combining claims 3 and 4 while removing alternatives and replacing the expression "obtained from" by "obtained from monomers comprising", to give new claim 7,
4. combining claims 3 and 4 while removing alternatives and splitting the optional component d) in two components, to give new claim 9.
5. renumbering claims 5-11 to give new claims 9-15,
6. renumbering claim 13 to give new claim 16.
7. adaptation of the description to the wording of the claims and correction of the citation number on page 2.

The replacement of "obtained from" by "obtained from monomers comprising" is based on the description as originally filed (page 11, last two paragraphs). The amendments consisting in combining claims and renumbering, as well as the removal of alternatives, do not introduce subject-matter which extends beyond the content of the application as filed. The amendments 1. to 3., 5. and 6. are therefore considered allowable (Article 34(2)(b) PCT).
The same applies to the adaptation of the wording of the description.
A basis for the splitting of the optional component d) into two components can be found in the description on page 8 or page 12, where it is stated that the radicals corresponding to the different components can be comprised alternatively or in combination ("contain repeating units of the formulae I and VI, and optionally II, III, IV, V **and/or** polyesterdiol radicals"). Polycarbonate or polylactone diols are comprised in the term "polyester diols". Therefore also amendment 4. is based in the original application and therefore considered allowable (Article 34(2)(b) PCT).

PWB-P2078_ATE_PCT-New_Claims

Photocrosslinkable polyurethanes

The present invention relates to a process for the production of solder masks on a printed circuit; to linear polyurethanes with selected diols; to those polyurethanes in which some or all of the carboxyl groups have been esterified with ethylenically unsaturated alcohol or epoxide; photocurable and optionally additionally thermally curable compositions which contain these polyurethanes; and materials coated with the cured and optionally structured composition.

US-4 794 133 describes acrylate-terminated polyurethanes polymerizable (curable) with UV radiation and obtained from diisocyanates and diols, for coating optical fibres.

EP-0 414 102 A2 describes modified isophorone diisocyanates, one of whose isocyanate groups contains a dihydroxyethylamino group as a diol component and the other of whose isocyanate groups contains an ethylenically unsaturated group covalently bonded via a bridge group. These monomers are used for the preparation of polyurethane elastomers, with which, inter alia, surfaces can be coated and then polymerized under the action of radiation.

WO 01/25306 describes radiation-polymerizable, linear polyurethanes obtained from aliphatic diisocyanates, aliphatic diols and monofunctional olefinically unsaturated compounds, which polyurethanes have terminal olefinic groups and are used as powder coating materials.

Radiation-polymerizable (curable), linear polyurethanes containing ethylenically unsaturated groups have already been proposed for the coating of surfaces, cf. EP-0 048 913 A1. The polyurethanes are prepared from diols, diisocyanates and a reaction product of bisphenols or alkylenedicarboxylic acids and glycidyl (meth)acrylates. The polymers contain no carboxyl groups and therefore cannot be developed with aqueous basic systems to give a structured surface after polymerization under a photomask. In order to avoid this disadvantage, the copolymers are formulated to give coating compositions which contain a copolymer with covalently bonded carboxyl groups. Reaction products are used for the preparation, which is complicated in terms of process engineering and often leads to nonreproducible results.

Radiation-polymerizable coating compositions comprising radiation-sensitive polyurethanes are described in EP-0 480 251 A1. The polyurethanes are prepared from diols, diisocyanates

and a reaction product of (meth)acrylic acid and polyols or bisepoxides, such as, for example, diglycidyl ethers of bisphenols, and are dispersed together with other ethylenically unsaturated prepolymers in water. These coating compositions are applied over the whole surface and cannot be developed with aqueous basic systems to give a structured surface.

WO 02/094904 describes linear polyurethanes which consist of a reaction product of a bisepoxide with an olefinically unsaturatured carboxylic acid as a diol component, a carboxylic acid having two hydroxyl groups as a further diol component and optionally other diols. They are used for coating and optionally structuring surfaces and they can be developed with aqueous alkaline media. A disadvantage of these systems is the prior preparation of the unsaturated diol component.

US-A-4 877 711 describes linear polyurethanes comprising residues of a diisocyanate, a carboxylic group containing diol and optionally a diol such as ethylene glycol or polyethylene glycol, whereby a part of the carboxylic groups is reacted with an epoxide compound comprising a carbon-carbon unsaturated bond. The polyurethanes are used in photosensitive coating compositions for the production of printing plates.

Polyurethanes which are polymerizable both under the action of actinic radiation and thermally and in which the radiation-sensitive or thermally polymerizable, olefinic groups are introduced into side chains after the polymerization of the polyurethane components, which have high radiation sensitivity for rapid polymerization or, in the presence of free radical initiators, also thermal sensitivity and additionally are soluble in aqueous alkaline media are not known. Furthermore, block copolymers having such polyurethane blocks are not known. Such a synthesis strategy and such block copolymers are, however, extremely desirable since, after their preparation, polyurethanes can be adjusted specifically with regard to acidity and content of olefinic groups and adapted to the respective requirements of the applications. In addition, a functional or easily functionalized building block for a modular system with other functional polymers is obtained, by means of which building block the properties thereof can be adapted in a variety of ways to processing and desired mechanical and physical properties of the end products.

The invention firstly relates to a process for the production of solder masks on a printed circuit as described in claim 1.

Linear polyurethanes used in the process comprise

a) at least one diisocyanate having 2 to 30 carbon atoms and

b) at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded.

The diisocyanates may be aliphatic, cycloaliphatic, aliphatic-cycloaliphatic, araliphatic or aromatic diisocyanates which preferably contain 2 to 20 and particularly preferably 2 to 16

carboxytetradecane, 1,2- or 2,3- or 3,4-dihydroxy-16-carboxyhexadecane, 1,2- or 2,3- or 3,4-dihydroxy-17-carboxylheptadecane, 1,2- or 2,3- or 3,4-dihydroxy-18-carboxyoctane, 1,3-dihydroxy-2-carboxymethylpropane, 1,4-dihydroxy-2-carboxymethylbutane, 1,5-dihydroxy-3-carboxymethylpentane, tartaric acid, 1,3-dicarboxy-2,3-dihydroxypropane, 1,4-dicarboxy-2,3-dihydroxybutane, 1,4-dihydroxy-2,3-dicarboxybutane, 1,4-dihydroxy-2-carboxycyclohexane and 1,4-dihydroxymethyl-2-carboxycyclohexane.

Preferred diols containing carboxyl groups are 1,2-dihydroxypropionic acid, 1,3-dihydroxy-2-carboxypropane, 1,2- or 1,3-dihdyroxybutyric acid, 1,4-dihydroxy-2-carboxybutane, 1,3-dihydroxy-2-methyl-2-carboxypropane, 1,5-dihydroxy-3-carboxypentane, 1,6-dihydroxy-3-carboxyhexane and tartaric acid. 1,3-Dihydroxy-2-methyl-2-carboxypropane and tartaric acid are particularly preferred.

The polyurethanes ~~according to the invention~~ may additionally contain

c) radicals of at least one aliphatic, cycloaliphatic or cycloaliphatic-aliphatic diol, or at least one oligomeric or polymeric oxaalkylene glycol, one polyesterdiol, polycarbonatediol or polylactonediol, or of a diol based on polybutadiene or polyisoprene having terminal hydroxyl groups.

The aliphatic diols may be linear or branched and contain preferably 2 to 18, more preferably 2 to 12 and particularly preferably 2 to 6 carbon atoms. Examples of aliphatic radicals (alkylene) have been given above for R_1. Some examples of preferred aliphatic diols are ethylene, 1,2- and 1,3-propylene, 1,2-, 1,3- and 1,4-butylene, 1,2-, 1,3-, 1,4- and 1,5-pentylene and 1,2, 1,3-, 1,4-, 1,5- and 1,6-hexylene glycol, heptanediols, octanediols, decanediols, tetradecanediols, hexadecanediols and octadecanediols. C_2-C_6Alkylenediols are particularly preferred.

The cycloaliphatic or cycloaliphatic-aliphatic radicals may be mononuclear rings or polynuclear linked, bridged or fused ring systems, the rings containing 3 to 12, preferably 4 to 8 and particularly preferably 5 or 6 ring carbon atoms. Examples of the latter are [2.2.1]bicycloheptane, [2.2.2]bicyclooctane and [1.0.0]tricyclodecane. Cyclic radicals are preferably substituted by two C_2-C_4hydroxyalkyl and particularly preferably by two hydroxymethyl. Examples of cycloaliphatic and cycloaliphatic-aliphatic radicals have been mentioned above for R_1. Some preferred examples of cycloaliphatic or cycloaliphatic-aliphatic diols are 1,3-dihydroxycyclopentane, 1,3- and 1,4-dihydroxycyclohexane, 1,4-

formula II may be, for example, 50 to 0.01 mol%, preferably 50 to 2 mol%, particularly preferably 50 to 20 mol% and very particularly preferably 50 to 30 mol%. The amount of the structural elements of the formulae III, IV, V and/or of polyesterdiols may be, for example, 0 to 49.99 mol%, preferably 0 to 48 mol%, particularly preferably 0 to 30 mol% and very particularly preferably 0 to 20 mol%. The molar percentages sum to 100 mol%. In the polyurethanes according to the invention, structural elements of the formula III may have been combined with oligomeric or polymeric diol radicals, in particular with structural elements of the formulae IV, V and radicals of polyesterdiols, so that, for example, in addition to structural elements of the formula II, 10 to 20 mol% of structural elements of the formula III and 0.01 to 10 mol% of structural elements of the formulae IV, V and radicals of polyesterdiols are contained.

The molecular weight (weight average Mw) may be, for example, from 2 000 to 150 000, preferably from 8 000 to 60 000, g/mol, measured by GPC using toluene as a standard.

The polyurethanes ~~according to the invention~~ may be random polymers or block polymers having blocks comprising structural elements of the formulae I and II and blocks comprising structural elements of the formulae I and III, of the formulae I and IV, of the formulae I and V, of the formula I and polyesterdiol radicals, or of the formulae I, III and IV or I, III and V and of the formulae I, III and polyesterdiol radicals.

The polyurethanes ~~according to the invention~~ may additionally be modified in a procedure in which isocyanate-terminated or correspondingly blocked (for example with hydroxymethyl acrylate) isocyanate-terminated polyurethanes are reacted subsequently with mono- or bishydroxyl-modified polymers. For such reactions, for example, the abovementioned polyoxaalkylene glycols and polyesterdiols are suitable. Other suitable polymers are, for example, poly(meth)acrylates whose terminal carboxyl groups have been modified with mercaptoethanol. In these polyurethanes according to the invention, the modifying polymer chains are bonded in the terminal position. Further suitable polymers are, for example, poly(meth)acrylates whose terminal carboxyl groups have been provided with thioglycerol with a diol function. In these polyurethanes, the modifying polymer chains are bonded in such a way that they link the polyurethane blocks to one another and form comb-like structures. Furthermore, hydroxyl-terminated polyurethanes according to the invention can be subsequently modified with isocyanate-terminated or correspondingly blocked (for example with hydroxymethyl acrylate) isocyanate-terminated polyurethanes, with the result that block

polyurethanes are obtained. Polyurethanes which can be used for this purpose are known or can be prepared by an analogous method, for example from diisocyanates and diols, as mentioned above, including the preferences. The polyurethanes differ from the polyurethanes according to the invention since they contain no diols having covalently bonded carboxyl groups. With such block copolymers, desired physical and mechanical properties can additionally be established in a controlled manner and adapted to specific applications.

(may be)

The ~~invention therefore also comprises~~ polyurethanes in the form of block copolymers having blocks of repeating structural elements of the formulae I and II and optionally III, IV, V and/or polyesterdiol radicals, and identical or different blocks of polyoxaalkylenediols, polyesterdiols, polyurethanes without pendant carboxyl groups, and poly(meth)acrylic acid.

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~~According to the invention,~~ ~~s~~alts of the polyurethanes are also included, for example alkaline earth metal (magnesium and calcium) and preferably alkali metal salts (sodium or potassium) and ammonium salts of ammonia or primary, secondary or tertiary C_1-C_{12}amines, for example methylamine, ethylamine, n-propylamine, n-butylamine, dimethylamine, diethylamine, di-n-propylamine, di-n-butylamine, triethylamine, tri-n-propylamine, tri-n-butylamine, piperidine and morpholine.

The preparation of the linear polyurethanes can be effected by processes known per se, which have been widely described for the polyurethanes in the relevant literature. Frequently, a procedure is adopted in which diols are initially taken in a suitable solvent, a catalyst (organic tin compounds, such as, for example, dibutyltin dilaurate) is added, the mixture is heated and then the isocyanate is slowly added over a relatively long period. The polyurethane obtained can be isolated or the reaction mixture can be used directly for the esterification of the carboxyl groups. Further details are given in the examples.

The polyurethanes ~~according to the invention~~ are outstandingly suitable for further modification with partial or complete esterification of the free carboxyl groups in the structural elements of the formula II, in order to provide photocrosslinkable polymers which, in the case of partial esterification or in combination with polymeric structural elements of polymers containing carboxyl groups, are moreover water-soluble. A particular advantage here is that the acidity (number of carboxyl groups) and the crosslinkability (number of olefinically unsaturated groups or degree of esterification) can be adjusted in one process step. For example, olefinically unsaturated alcohols or glycidylvinyl compounds can be used for the

esterification.

The glycidylvinyl compounds used according to the invention each have an epoxide radical and a vinyl radical, an acrylate radical being preferred as the vinyl radical. Examples of such glycidylvinyl compounds are also to be found, inter alia, in US 4,927,884, column 12, line 19 et seq. Organic radicals substituted by a vinyl group are, for example, aliphatic, alicyclic or aromatic radicals substituted by a vinyl group. The aliphatic, alicyclic or aromatic radicals may be optionally substituted alkylene, such as C_1-C_8alkylene, optionally substituted cycloalkylene, such as C_5-C_8cycloalkylene, optionally substituted arylene, such as phenylene or naphthylene, or optionally substituted alkenylene, such as C_2-C_8alkenylene. Suitable substituents for the aliphatic, alicyclic or aromatic radicals are, for example, hydroxyl groups, C_1-C_8alkyl groups and C_1-C_8alkoxy groups. The aliphatic, alicyclic or aromatic radicals are preferably unsubstituted.

Compounds suitable for the esterification are in particular low molecular weight, olefinically unsaturated alcohols and glycidyl esters of low molecular weight olefinically unsaturated carboxylic acids. In the context of the invention, low molecular weight may mean alcohols and carboxylic acids having 3 to 8 and preferably 3 to 6 carbon atoms. Some preferred examples are allyl alcohol, crotonyl alcohol, acrylic acid, methacrylic acid and crotonic acid. Glycidyl (meth)acrylate is particularly preferred.

The ~~invention furthermore relates to~~ linear, crosslinkable polyurethanes comprise ~~ing~~

a) at least one diisocyanate having 2 to 30 carbon atoms and

b) at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded, and some or all of said carboxyl groups have been esterified with an olefinically unsaturated C_3-C_8alcohol or with the glycidyl ester of an olefinically unsaturated C_3-C_8carboxylic acid, and

c) optionally at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded.

The linear, crosslinkable polyurethanes ~~according to the invention~~ may additionally contain

d) radicals of at least one aliphatic, cycloaliphatic or cycloaliphatic-aliphatic diol, of at least one oligomeric or polymeric oxaalkylene glycol, of a polyesterdiol, polycarbonatediol or polylactonediol.

The linear, crosslinkable polyurethanes ~~according to the invention~~ may additionally comprise block copolymers as described above.

The degree of esterification may be, for example, 0.1 to 100, preferably 1 to 90 and particularly preferably from 5 to 80, % of the carboxyl groups. The degree of esterification can be determined via the acid number. The acid number may be, for example, 0.2 to 1.4 and preferably 0.6 to 1.4 mol KOH per kg polyurethane (solid), measured by titration with KOH.

Otherwise, the developments, embodiments and preferences as have been indicated above for the linear and uncrosslinkable polyurethanes are applicable.

In a preferred embodiment, the linear, crosslinkable polyurethanes contain repeating units of the formulae I and VI, and optionally II, III, IV, V and/or polyesterdiol radicals,

$-(O)CN-R_1-NC(O)-$ (I),

$-O-R_2(COOH)_m-O-$ (II),

$-O-R_3-O-$ (III),

$-O-(R_4-O)_n-$ (IV),

$Y-(CH_2-CH=CH-CH_2)_x-Y$ (V)

$-O-R_2(COOR_5)_m-O-$ (VI)

in which R_1, R_2, R_3, R_4, Y, m, n and x have the abovementioned meanings, including the preferences, and R_5 is allyl, crotonyl, $CH_2=CH_2-C(O)-O-CH_2-CH(OH)-CH_2-$ or $CH_2=C(CH_3)-C(O)-O-CH_2-CH(OH)-CH_2-$.

The crosslinkable polyurethanes can be obtained by esterifying the linear polyurethanes. In order to avoid secondary reactions, inhibitors may be added to the reaction mixture. The reaction temperature is preferably in the range from 70 to 150°C. In the esterification, it is also possible to use alkali metal alcoholates. Expediently, resulting water of reaction is removed during the reaction. Glycidyl esters are as a rule more reactive and are therefore preferably used. Further details are to be found in the examples.

Depending on molecular weight, the crosslinkable polyurethanes according to the invention are liquid to solid material which are soluble in organic solvents and water and can be crosslinked both under the action of either heat or radiation, or heat and radiation. The polyurethanes can therefore also be used in different areas, for which purpose they can be formulated according to the desired applications.

(process of the) (uses)
The invention ~~furthermore relates to~~ a composition comprising

a) crosslinkable polyurethane ~~according to the invention~~ described above,
b) an initiator for the thermal crosslinking of the olefinic groups, or
c) a photoinitiator, or
d) an initiator for the thermal crosslinking of the olefinic groups and a photoinitiator, and
e) optionally a diluent.

The composition ~~according to the invention~~ may additionally contain polymeric binders. Examples of such binders are polyacrylates and Ripoxy polymers (Showa Highpolymer Co. Ltd.). The binders may be contained in an amount of 5 to 90, preferably 10 to 50, % by weight, based on the composition.

For the thermal crosslinking, a free radical initiator, for example organic azo compounds, such as azobisisobutyronitrile, or peroxides, such as diacylbenzoyl peroxide, is incorporated into the polyurethane. The amount may be 0.01 to 5% by weight, based on the composition.

A photopolymerization initiator is added to the composition according to the invention if the composition is crosslinked (cured), for example, by exposure to UV light. Typical examples of photopolymerization initiators are bezoin and benzoin alkyl ethers, such as benzoin, benzil, benzoin methyl ether, benzoin ethyl ether, benzoin n-propyl ether, benzoin n-butyl ether, benzoin isopropyl ether and the like; benzophenones, such as benzophenone, p-methylbenzophenone, Michler's ketone, methylbenzophenone, 4,4'-dichlorobenzophenone, 4,4-bisdiethylaminobenzophenone and the like; acetophenones, such as acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone, 1,1-dichloroacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2-methyl[4-(methylthio)phenyl]-2-morpholino-1-propanone, N,N-dimethylaminoacetophenone and the like; thioxanthanone and xanthones, such as 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2-chlorothioxanthone, 2,4-diisopropylthioxanthone and the like; anthraquinones, such as anthraquinone,

The composition ~~according to the invention~~ may also contain an epoxide curing agent. This serves for crosslinking the epoxy groups during heating, so that the protective film produced using the composition according to the invention has good heat resistance, moisture resistance and electrical properties. Examples of said curing agents are s-triazine compounds, such as melamine, ethyldiamino-s-triazines, 2,4-diamino-s-triazine, 2,4-diamino-6-tolyl-s-triazine, 2,4-diamino-6-xylyl-s-triazine, and derivatives thereof. Guanidine compounds, such as guanidine, acetoguanidine, benzoguanidine, 3,9-bis[2-(3,5-diamino-2,4,6-triazaphenyl)ethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane and the like, s-triazine compounds thereof are latent epoxide curing agents of the epoxy resins. They result in better adhesion between protective film and substrate. Consequently, corrosion and colour changes of the copper in the production of circuit boards can be prevented. Imidazole compounds likewise accelerate the adhesion. Moreover, polyamines, such as diaminodiphenylmethane, m-phenylenediamine, diaminodiphenyl sulphone, cyclo-hexylamine, m-xylylenediamine, 4,4'-diamino-3,3'-diethyldiphenylmethane, diethylenetriamine, tetraethylenepentamine, N-aminoethylpiperazine, isophoronediamine, dicyandiamide, urea, urea derivatives, polybasic hydrazines and the like, organic acid salts thereof and/or epoxy adducts thereof; tertiary amines, such as trimethylamine, triethanolamine, N,N-dimethyloctylamine, N,N-dimethylaniline, N-benzyldimethylamine, pyridine, N-methylpyridine, N-methylmorpholine, hexamethoxymethylmelamine, 2,4,6-tris(dimethylaminophenol), N-cyclohexyldimethylamine, tetramethylguanidine, m-aminophenol and the like; organic phosphines, such as tributylphosphine, triphenylphosphine, tris-2-cyanoethylphosphine and the like; potassium salts such as tri-n-butyl(2,5-dihydroxyphenyl)phosphonium bromide, hexadecyltributylphosphonium chloride and the like; quaternary ammonium salts, such as benzyltrimethylammonium chloride, phenyltrimethylammonium chloride, benzyltrimethylammonium bromide and the like; and photocationic polymerization catalysts, such as diphenyliodonium tetrafluoroborate, triphenylsulphonium hexafluoroantimonate, 2,4,6-triphenylthiopyrylium hexafluorophosphate, Irgacure 261 (product of Ciba Geigy) and the like, are also suitable. The abovementioned epoxide curing agents can be used alone or in combination.

The epoxide curing agents are expediently used in weight ratios of the polyepoxide to epoxide curing agent of 95:5 or less, preferably 98:2 or less. As a result of the presence of the epoxide curing agent in the abovementioned amount, sufficient crosslinking takes place so that desired water resistance and heat resistance are obtained, making the composition

~~according to the invention~~ particularly preferred compared with the compositions known to date.

The composition ~~according to the invention~~ can moreover contain inorganic and/or organic fillers in order to improve the adhesion properties or hardness of mouldings or layers. The inorganic fillers are preferably selected from the group consisting of barium sulphate, barium titanate, powdered silica, finely powdered silica, amorphous silica, talc, chalk, magnesium carbonate, calcium carbonate, alumina, aluminium hydroxide, mica powder and the like. The composition ~~according to the invention~~ preferably contains up to 60% by weight, preferably 5-40% by weight, of inorganic fillers.

Allyl compounds, such as diallyl phthalate prepolymer, diallyl isophthalate prepolymer and the like, can be added as organic fillers. By adding the organic fillers, it is also possible to increase the chemical stability. The composition according to the invention may contain up to 30% by weight and particularly preferably up to 20% by weight of organic fillers per 100% by weight of the prepolymer curable by exposure to light. Examples are Daiso Dap and Daiso Isodap, produced by Osaka Soda AG and having an average molecular weight of 2 000-30 000 g/mol, and diallyl isophthalate prepolymers having an average molecular weight of 5 000-20 000 g/mol.

The composition ~~according to the invention~~ may also contain additives, such as dyes, pigments, lubricants, mould release agents, thickeners, antifoams, levelling agents, thermal polymerization inhibitors or antioxidants. Possible dyes are phthalocyanine blue, phthalocyanine green, iodine green, disazo yellow, crystal violet, titanium oxide, carbon black, naphthalene black and the like. Possible thermal polymerization inhibitors are hydroquinone, hydroquinone monomethyl ether, tert-butylcatechol, pyrogallol, phenothiazine and the like. Suitable thickeners are, for example, orben, penton, montmorillonite and the like. Suitable antifoams are, for example, fluorosilicone-like, fluoride-like or polymer-like antifoams.

The crosslinkable polyurethanes can be employed, for example, as thermosetting moulding materials with the use of customary shaping methods. Depending on the thickness of the mouldings, the crosslinking can be effected thermally and/or by means of radiation and curing can thus be achieved. Additives by means of which the processing and properties can be influenced may be added to the moulding materials. Customary additives are, for

pattern serving as a protective film being obtained on the circuit board. The heat treatment for postcuring can be carried out at 100 to 200°C, preferably 120 to 150°C.

Particularly suitable radiation sources are UV sources, for example high-pressure mercury lamps and xenon lamps or lasers, including UV lasers.

The choice of the developer liquid depends substantially on the acidity of the crosslinkable polyurethane. At a high acidity, aqueous-alkaline developers are advantageously used. Examples of aqueous alkaline solutions are aqueous solutions comprising potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate, sodium phosphate, sodium silicate, ammonia, amines and the like and/or aqueous solutions comprising a surfactant. At low acidity, organic developer liquids, for example cyclohexanone, xylene, tetramethylbenzene, butylcellosolve, butylcarbitol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether, cellosolve acetate, propanol, propylene glycol, trichloroethane, trichloroethylene, γ-aminobutyrolactone, modified trichloroethane [Eterna IR (product of Asahi Kasei Kogyo), Squone EX-R (product of Toa Gosei Kagaku), Kanden Triethan SR-A (product of Kanto Denka Kogyo), Resisolve V-5 (product of Asahi Glass)], are expediently used.

The composition ~~according to the invention~~ is preferably sold in a set comprising two containers A and B. Those components which react together can thus be separated so that the container A contains the crosslinking agents (polyepoxide compounds) curable by the action of heat and the container B contains the other ingredients of the composition, or the container A contains a polycarboxylic acid or a carboxylic anhydride if the polyurethane has no carboxyl groups or only a few carboxyl groups.

Mouldings or coatings of the composition ~~according to the invention~~ have outstanding physical, mechanical and electrical properties, for example hardness, thermal shock resistance and electrical resistance measured under humid conditions and flexural strength.

Optionally photostructured coatings of the composition ~~according to the invention~~ are distinguished by their adhesive strength, elongation at break, hardness and resistance to treatment baths. Furthermore, high photoreactivity and hence short exposure times during exposure to, preferably, UV light, coupled with high resolution, are achieved.

The invention also relates to mouldings of the cured composition, ~~according to the invention/~~

The invention furthermore relates to materials in which at least one surface is coated with a cured, optionally photostructured composition according to the invention, described below.

The invention also relates to
linear polyurethanes as described above containing a polyesterdiol, a polycarbonatediol, a polylactonediol or a diol based on polybutadiene or polyisoprene;
crosslinkable, linear polyurethanes as described above containing a polyesterdiol, a polycarbonatediol, a polylactonediol or a diol based on polybutadiene or polyisoprene; and a composition containg a crosslinkable, linear polyurethanes as described above containing a polyesterdiol, a polycarbonatediol, a polylactonediol or a diol based on polybutadiene or polyisoprene.

The examples which follow explain the invention in more detail.

Abbreviations:

ACA 250	Polyacrylate resin, Daicel Chemical Industries, LTD
MPA=PMA	Methoxypropylacetate
MP	Methoxypropanol
Cr-Hex-CEM	Chromium(III) 2-ethylhexanoate
TMPTA	Trimethylolpropane triacrylate (Cray Valley)
Ebecryl 160	Poly[oxy-1,2-ethanediyl-alpha,hydro-omega-[(1-oxo-2-propenyl)oxyl]] ether and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (3:1), (UCB)
Irgacure 907	2-Methyl-1-(4-methylthio)phenyl-2-morpholino-1-propanone (Ciba)
Orasol blue GN	Phthalocyanine dye, Ciba
Quantacure ITX	2,4-Isopropylthioxanthone, Rahn
Silbond FW 600AST	SiO_2, Quartzwerk Frechen
Dyhard UR 200	Substituted aromatic urea (Rahn)
Tego 900	Polysiloxane (Tego)
Syloid 161	Amorphous silica, SiO_2 (Grace)
DER 331	Bisphenol-A epoxy resin (Dow)
Lionol Green 2Y-301	Phthalocyanine dye (Toyo)

Claims:

1. A process for the production of solder masks on a printed circuit, comprising the steps
   a) coating of a circuit board with the photocrosslinkable composition comprising a linear, crosslinkable polyurethane A1 obtained from monomers comprising
   i) at least one diisocyanate having 2 to 30 carbon atoms,
   ii) at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded, and some or all of said carboxyl groups have been esterified with an olefinically unsaturated C_3-C_8-alcohol or with the glycidyl ester of an olefinically unsaturated C_3-C_8carboxylic acid, and
   iii) optionally at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded,
   A2) an initiator for the thermal crosslinking of the olefinic groups, or
   A3) a photoinitiator, or
   A4) an initiator for the thermal crosslinking of the olefinic groups and a photoinitiator, and
   A5) optionally a diluent,
   b) drying of the layer on the substrate,
   c) imagewise exposure of the dried layer under a negative photomask or by means of laser inscription,
   d) treatment of the coated layer with a developer for removing the unexposed parts, and
   e) optionally heat-curing of the developed layer.

2. A process according to claim 1, wherein the photocrosslinkable composition additionally contains
   A6) a polymeric binder.

3. A process according to claim 1 or 2, wherein the photocrosslinkable composition additionally contains
   A7) crosslinking agents which are capable of reacting with the carboxyl groups.

4. A process according to claim 3, wherein the crosslinking agent is a polyepoxide ha-

ving at least 2 epoxide groups in the molecule.

5. A process according to claim 4, wherein the photocrosslinkable composition additionally contains a polycarboxylic acid or carboxylic anhydrides for the thermal crosslinking of the polyepoxides.

6. A process according to claim 1, wherein the photocrosslinkable composition comprises a linear, crosslinkable polyurethane obtained in additionally using as monomer
   iv) at least one aliphatic, cycloaliphatic or cycloaliphatic-aliphatic diol, or at least one oligomeric or polymeric oxaalkylene glycol, a polyesterdiol, a polycarbonatediol, a polylactonediol or a diol based on polybutadiene or polyisoprene.

7. A linear, crosslinkable polyurethane obtained from monomers comprising
   a) at least one diisocyanate having 2 to 30 carbon atoms,
   b) at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded, and some or all of said carboxyl groups have been esterified with an olefinically unsaturated C_3-C_8alcohol or with the glycidyl ester of an olefinically unsaturated C_3-C_8carboxylic acid,
   c) a polyesterdiol, polycarbonatediol, polylactonediol or a diol based on polybutadiene or polyisoprene, and
   d) optionally at least one aliphatic or cycloaliphatic diol having 2 to 30 carbon atoms, to whose carbon chain at least one carboxyl group is covalently bonded.

8. A linear, crosslinkable polyurethane according to claim 7, which is obtained from additionally using as monomer
   e) at least one aliphatic, cycloaliphatic or cycloaliphatic-aliphatic diol, or at least one oligomeric or polymeric oxaalkylene glycol.

9. A composition comprising
   a) a crosslinkable polyurethane according to claims 8 or 9,
   b) an initiator for the thermal crosslinking of the olefinic groups, or
   c) a photoinitiator, or
   d) an initiator for the thermal crosslinking of the olefinic groups and a photoinitiator, and

e) optionally a diluent.

10. A composition according to claim 9, which additionally contains
    f) a polymeric binder.

11. A composition according to claims 9 or 10, which additionally contains crosslinking agents which are capable of reacting with the carboxyl groups.

12. A composition according to claim 11, wherein the crosslinking agent is a polyepoxide having at least 2 epoxide groups in the molecule.

13. A composition according to claim 12, which additionally contains a polycarboxylic acid or carboxylic anhydrides for the thermal crosslinking of the polyepoxides.

14. A moulding comprising the cured composition according to any of claims 1 and 9 to 13.

15. A material in which at least one surface is coated with a cured, optionally photostructured composition according to any of claims 9 to 13.

16. A use of the composition according to any of claims 9 to 13 as moulding material for the production of mouldings, as coating material for coating surfaces, as adhesive for bonding materials or as an etch resist or solder masks, for gap filling or filling of cavities or as a liquid dielectric in the production of circuit boards.